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December 6, 1994

Kathy Kuivila
U.S. Geological Survey
2800 Cottage Way
Sacramento, CA 95825

Dear Ms. Kuivila:

A meeting for the toxics briefing paper review team has been set for December 16, 1994 at 9:00 a.m. in Room 1147-C1 of the Resources Building located at 1416 Ninth Street. The purpose of this meeting is to ensure the briefing paper addresses each agency's concerns regarding toxics in the Estuary. The attached draft sections of the briefing paper are being provided for your review prior to the meeting. These represent the initial effort to provide the most current information available regarding toxics in the Bay/Delta. If you have any questions about the briefing paper, please call me at (916) 657-2666 or contact Victor Pacheco of the BDOC staff at the same phone number.

Sincerely,

Steve Yaeger

Steve Yaeger
Deputy Executive Officer

Attachment

TOXIC REPORT SCHEDULE

November, 1994	Draft Ambient Toxicity Chapter submitted to Review Team
	Draft Pesticides Chapter submitted to Review Team
December, 1994	Draft Species Effects Chapter submitted to Review Team
	Review Team Meeting
	Revised report submitted to Review Team
January, 1995	Review Team Meeting
	Report modifications
	WPCG review / Oversight Committee
Feburary, 1995	Process modifications of Draft Report
	Peer Review and Federal Agency Review
March, 1995	Process Modifications / Reproduction / Distribution
	Final Review by WPCG and Federal Policy makers
	Final Modifications and Reproduction
APRIL, 1995	**Deliver to Council**
April, 1995	Briefing to Council

The Effects of Toxic Substances in Fish, Wildlife, and Plant Resources of the Bay-Delta Estuary

<u>Outline</u>

I. Introduction
   A. The Bay-Delta Estuary
      1. Fish, Wildlife, and Plant Resources
      2. Pollutant Sources
      3. Potential Effects of Pollutants on Natural Resources
      4. Scope of this Report Defined

II. Pollutants in the Bay-Delta Estuary
   A. Pollutant Types
      1. Trace Elements
      2. Pesticides
      3. Organic Compounds
   B. Pollutant Sources
      1. Existing
      2. Potential
      3. Point Source vs. Non-Point Source
   C. Geographical Distribution (Graphics)
      1. Industrial Sources
      2. Oil Refineries
      3. Municipal Waste Disposal Sites
      4. Agricultural Drains
      5. Superfund Sites

III. Toxic Effects of Pollutants in the Bay-Delta Estuary
   A. Impacts to Natural Resources (Historical/Existing)
      1. Fish
      2. Wildlife
      3. Plants

IV. Pollution Assessment, Evaluation, and Control
   A. Water Quality Control Plans
   B. Research and Monitoring Programs
   C. Current Status

V. Conclusion

Pesticides

Determination of pesticide toxicity in Estuary waters has been largely ignored until fairly recently. This has been reflected in lack of analytical monitoring for these chemicals in Bay and Delta waters, as well as in lack of toxicity testing of these waters. However, as a result of studies that suggested that pesticides were adversely affecting water quality in the Estuary and its tributaries (see, for example, Bailey *et al.* 1994; Finlayson *et al.* 1993; Foe and Sheipline 1993; Foe and Connor 1991; Norberg-King *et al.* 1991; Foe and Connor 1989), CDF&G initiated the process of producing water quality criteria for pesticides of interest. Criteria have been developed for molinate and thiobencarb (Harrington 1990), carbofuran (Menconi and Gray 1992), methyl parathion (Menconi and Harrington 1992b), and chlorpyrifos (Menconi and Paul 1994). A draft document for diazinon has also been completed (Menconi and Cox 1994). Values of 0.5 and 0.08 μg/L were recommended for carbofuran and methyl parathion, respectively, to protect aquatic life. An interim value of 0.02 μg/L was recommended for chlorpyrifos and diazinon concentrations protective of acute and chronic toxicity were 0.08 and 0.04 μg/L, respectively.

need transition — Does all pesticides come from Sac River?

Discharge from rice culture generally enters the Sacramento River upstream of Sacramento. However, in years of high flow, discharge from Colusa Basin Drain may be diverted into the Yolo Bypass and enter the River via Prospect Slough, downstream of Sacramento. Rice discharge is significant because, under certain flow conditions, input from Colusa Basin Drain alone can account for approximately 25 percent of the total flow of the Sacramento River (Cornacchia et al. 1984). Significant inputs also enter the River from Butte and Sacramento Sloughs. Because of the comparatively large component rice return flows contribute to the overall flow of the Sacramento River, the capacity for dilution of incoming toxicants is relatively low.

Monitoring of the Delta for the rice herbicides molinate and thiobencarb was not initiated until 1985, even though large fish kills associated with agricultural drainage from rice culture occurred several years earlier (State Water Resources Control Board 1990). Measured concentrations of molinate and thiobencarb in 1985 suggested that concentrations toxic to *Neomysis mercedis* were approached in the upper Delta (Bailey 1993). In subsequent years, efforts by rice farmers to correct this problem led to

rapidly increasing on-field holding times reduced concentrations of these pesticides in the Delta to levels below those associated with toxicity, although molinate and thiobencarb have been detected in the Delta as recently as 1993 (K. Kuivila, USGS, personal communication). In the years between 1982 and 1985, extrapolation from measured concentrations in Colusa Basin Drain suggests that the toxic threshold for *N. mercedis* could have been exceeded by a factor of nearly six (Bailey 1993). Analytical data for earlier years are not available but comparisons of application rates and river flows suggests that discharge concentrations back to 1978 and 1981 were at least as high as those present between 1982 and 1985 for molinate and thiobencarb, respectively (see Table 1, Appendix A).

Other pesticides applied to rice have also been associated with toxicity. Bailey *et al.* (1994) showed that five pesticides out of approximately 20 applied to rice for at least five years between 1970 and 1989 were negatively correlated with striped bass recruitment and, in fact, could explain nearly 90 percent of the variation in recruitment during this period. The pesticides were bufencarb (now discontinued), carbofuran, methyl parathion, molinate, carbaryl, and MCPA. With the exception of molinate and MCPA, these pesticides are cholinesterase inhibitors and would be expected to exert additive toxicity. Since most of these pesticides were applied in conjunction with each other, there could have been additive effects or effects on food organisms in addition to direct effects on striped bass early life stages. One pesticide in particular, bufencarb, exhibited extremely high toxicity to striped bass embryos and larvae, with acute LC50s of approximately 0.1 μg/L. At this level of toxicity, a daily input of 2400 g would be sufficient to poison the Sacramento River at a flow rate of 10,000 cfs. This would equate to approximately 150 lbs. over a 30-day period.

Application of carbofuran and methyl parathion to rice increased in 1980-1982 as bufencarb was being phased out. Applications to rice and Sacramento River flows between 1970 and 1988 are shown in Table 2, Appendix A. Although the applications have been significant, monitoring of carbofuran concentrations was not initiated until 1987. In that year, concentrations as high as 2.1 μg/L were detected in the Sacramento River during rice season (Menconi and Gray 1992). This value is clearly in excess of the water quality criteria of 0.5 μg/L recommended by DF&G (Menconi and Gray 1992). Based on application and flow rates, it is likely that 2.1 μg/L was exceeded annually between 1980 and 1987 and 0.5 μg/L was exceeded back through

Explain what these concentrations might mean for striped bass, salmon, etc smelt

1977. More restrictive use requirements reduced concentrations in the River to ≤ 0.5 μg/L by 1991 (Menconi and Gray 1992). Monitoring in the River and Delta between 1990 and 1992 by USGS suggests that carbofuran discharged from rice still reaches the Delta in trace concentrations (Kuivila *et al.* 1992). These data also suggested that Delta inputs of this pesticide, primarily from alfalfa, may also be significant.

Intermittent monitoring of methyl parathion concentrations in the Colusa Basin Drain and Sacramento River has occurred since 1980. In 1988 concentrations as high as 0.32 μg/L were detected in the Sacramento River. This value exceeds the recommended water quality criteria of 0.08 μg/L for this pesticide and also exceeds the acute LC50 values for *Daphnia magna* and *Neomysis mercedis* (Menconi and Harrington 1992b). Based on applications and flow rates (Table 2), River concentrations could have exceeded 0.32 μg/L in four of the nine years between 1980 and 1988. Using similar reasoning, the water quality criterion would have been exceeded in 15 of the 19 years between 1970 and 1988 (all of the years after 1976). Menconi and Harrington (1992b) also concluded that levels of this pesticide could have exceeded the criterion during the early 1980s. Their reasoning was based on a 25 percent contribution from Colusa basin Drain to the Sacramento River and measured concentrations of 3.7 μg/L in Colusa Basin Drain. This could have resulted in concentrations of up to 0.94 μg/L in the Delta. More recent monitoring data for 1990 sugggest that more restrictive management practices have decreased River concentrations of methyl parathion to ≤ 0.1μg/L (Menconi and Harrington 1992b).

The fragile relationship between management practices and off-site movement of pesticides from rice culture is shown in the following table (data from DPR 1994).

Pesticides Transported in the Sacramento River Past Sacramento (kg)

Year	Molinate	Thiobencarb
1988	3194	68.1
1989	1984	11.4
1990	3204	51.2
1991	99	0
1992	57	0
1993	2007	0

For comparison, an estimated 18,465 kg molinate was transported in 1982.

In 1991 and 1992, loadings of these pesticides in the Sacramento River decreased by over an order of magnitude from levels seen in previous years due to the new management plans. However, in 1993, emergency releases from treated fields prior to completion of the on-field holding time requirements resulted in the highest loadings to the River in five years. In fact, the loadings to the River were even higher than shown in the table since flows from Colusa Basin Drain, the most important source of rice pesticides to the Sacramento River, were diverted into the River downstream of DPR's monitoring point for rice pesticides (DPR 1994). Based on concentration and flow data in Colusa Basin Drain given in DPR (1994), a conservative estimate of additional loadings into the Sacramento River would be 1550 and 80 kg of molinate and thiobencarb, respectively. As an example of the efficiency of the required holding times, Regional Water Board staff compared the toxicity of samples collected from discharges from fields undergoing emergencey releases and from fields that had reached the required holding times (Schnagl and Wyels 1993). Water samples from fields that had complied with the required holding times were not toxic while nine of ten tailwater samples collected from fields undergoing emergency releases were acutely toxic to *C. dubia.*

Pesticides entering the Sacramento-San Joaquin system are also associated with other types of agriculture, discharges from municipal sewage treatment plants and storm water run-off. In two years of sampling the Delta, the three pesticides responsible for most of the observed toxicity were carbofuran, chlorpyrifos, and diazinon (Bailey *et al.,* unpublished data). These pesticides can occur in locally high concentrations in smaller waterbodies or across large quantities of water moving through the Delta during major storm events. Selected samples that exhibited toxicity and the associated pesticide concentrations are shown in the following table. All of the samples were acutely toxic to *C. dubia* and Toxicity Identification Evaluations were performed to determine the cause of toxicity.

Sample Site	Date	Pesticide	Concentration (μg/L)
French Camp Slough	3-23-94	chlorpyrifos	1.2
Paradise Cut	4-27-94	carbofuran	9.4
Paradise Cut	4-30-94	carbofuran	7.0
Paradise Cut	7-12-94	chlorpyrifos	0.6

Foe and Sheipline (1993) monitored watersheds in the Sacramento-San Joaquin Basin associated with orchards for toxicity during the dormant spray season between 13 January and 27 February. A total of 11 sites were monitored over 7 sampling events during this period. At least one sample collected from 9 of the 11 sites produced ≥ 50 percent mortality in *C. dubia.* Two, or more, samples collected from five of the sites produced total mortality in *C. dubia.* Of the 25 samples that exhibited significant mortality, diazinon was present in 22 samples at concentrations that exceeded the acute water quality criterion proposed by CDF&G (Menconi and Cox 1994). The median value was approximately 7 times the criterion, but concentrations as high as 6.8 µg/L (over 80 times the criterion) were reached. 21 of the samples contained concentrations that have been shown to cause acute mortality in *C. dubia* and six of the samples contained diazinon at concentrations lethal to *N. mercedis.*

An example of movement off-site into local receiving waters during irrigation and precipitation events is shown in a CDF&A study on diazinon applied in the lower American River watershed (Segawa and Powell 1989). In a three-year program designed to eradicate the Japanese beetle, it was found that most of the diazinon was confined to upper layers of soil and thatch, but that significant off-site movement in irrigation water and stormwater run-off occurred. Concentrations as high as 73 µg/L occurred in creeks receiving irrigation run-off and a concentration of 82 µg/L were recorded in local streams following rainfall events. Rainfall events as low as 0.4-0.6 cm were sufficient to move significant quantities off-site. Mass discharge rates of 7.8 gm/hr were recorded during irrigation and as high as 24 gm per hr during rainfall events. During rainfall events, discharge rates as high as 5100 µg/sec were measured. Following a rainfall event in Nov 1993, diazinon concentrations at nine sampling sites ranged between 0.4 and 44 µg/L. These values are from 1 to 110 times the acute LC50 for *C. dubia* and all exceed the DF&G draft criteria for diazinon. The median concentration was 2.9 µg/L, 7.25 times the LC50 for *C. dubia* and 2.4 times the LC50 for *N. mercedis.* In spring 1984, concentrations in the streams ranged between 0.2 and 82 µg/L, with a median of 4.9 µg/L. Measurements in Arcade Creek in fall 1984 during irrigation were between 0.7 and 11 µg/L, with a median of 6.4 µg/L. During rainfall events, concentrations reached 21 µg/L, 52 times the LC50 for *C. dubia.* Although less pesticide was applied in 1985 and 1986, concentrations still reached 2 and 27 µg/L in Arcade Creek in 1985 during irrigation and run-off periods, respectively. In 1986, rainfall events produced in-stream concentrations of up to 4.2 μg/L.

Using the fall (Aug - Oct) treatments as an example, Segawa and Powell (1989) estimated that an average of approximately 50 gm/day was leaving the treatment areas via waterways, with peaks of up to 200 gm/day. Assuming a uniform discharge rate, 50 gm/day would have been sufficient to contaminate a flow rate of 51 cfs at the approximate *C. dubia* LC50 of 0.4 μg/L. During precipitation events, up to 24 gm/hr was estimated to leave the treatment areas via waterways (18 gm/hr in one creek!). Using similar reasoning, this amount would render a flow rate of 600 cfs acutely toxic to *C. dubia* or cause a flow of 3000 cfs to exceed the DF&G acute criterion for diazinon.

In the fall 1983 treatment, there were nine confirmed bird kills (no numbers given) associated with the diazinon treatment (Segawa and Powell 1989).

In the spring of 1993, Hansen and Associates (1994) investigated toxicity associated with stormwater in the San Lorenzo Creek watershed which enters San Francisco Bay just north of Hayward. Samples were collected from 3-5 sites in the watershed following three precipitation events. Diazinon concentrations at the sites ranged between 0.74 and 2.9 μg/L for samples collected 16 March, between 0.82 and 2.9 μg/L for samples collected 17-21 March, and between 0.08 and 0.46 μg/L in samples collected 7 April. With the exception of the sample that contained 0.08 μg/L, all of the measured concentrations exceeded values associated with acute toxicity in *C. dubia* and two of the values exceeded the acute LC50 for *N. mercedis.* All of the values exceeded the proposed CDF&G acute and chronic water quality criteria for diazinon.

In fall of 1994, stormwater samples were collected from creeks and sumps discharging into the lower Sacramento and American Rivers, and also into the lower San Joaquin River (Bailey *et al.* unpublished data). Samples collected from Arcade, Elder, and Strong Ranch Creeks exhibited acute toxicity. In all cases, toxicity was removed by treatment with piperonyl butoxide, a biochemical that inhibits the toxicity of metabolically activated organophosphorous pesticides. Diazinon was found at acutely toxic concentrations in all three creeks and chlorpyrifos was found at acutely toxic concentrations at 1 of the 3 sites. In one of the two sumps, diazinon and chlorpyrifos were both present at acutely toxic concentrations, but metals also contributed to toxicity. In the remaining sump, toxicity was driven by high zinc concentrations. In sites that drained into the San Joaquin River,

Kuivila (1994) tracked diazinon concentrations in the Sacramento River at Sacramento and in the San Joaquin River at Vernalis prior to and during rainfall events in early February 1993. On the Sacramento River, it was found that pulses of diazinon moved past the City of Sacramento 1-3 days after each rainfall event. Each pulse lasted 4-5 days. Diazinon peaks in the River were approximately 0.4 and 0.2 μg/L, compared with pre-event concentrations of 0.03-0.05 μg/L.

Kuivila (1993) tracked the first Sacramento River diazinon pulse downstream into the Estuary. Her data suggest that diazinon concentrations peaked at Rio Vista and Chipps Island approximately 1- and 3 days after the pulse was recorded at Sacramento. Peak concentrations at these sites were 0.3 and 0.2 μg/L, respectively. It took an additional three days for the peak (now approximately 0.1 μg/L) to reach Martinez. The decreasing concentrations were due to tidally induced mixing. In addition, the peaks broadened as the pulse moved downstream. At Sacramento, concentrations exceeded 0.1 μg/L for five days, compared with 8 days at Chipps Island. All of these concentrations exceeded the acute diazinon criterion proposed by DF&G.

In contrast to the Sacramento River, diazinon concentrations at Vernalis responded in bimodal peaks following the first rainfall event, suggesting upstream as well as local sources of diazinon (Kuivila 1994). Background concentrations of diazinon at Vernalis prior to and between storm events were approximately 0.1 μg/L. In the first event (1.8 inches of rain), concentrations rose above 0.3 μg/L, with peaks of 0.8 and 1.1 μg/L for 8 days. The two subsequent events were much smaller, 0.7 and 0.6 inches, and resulted in 48- and 24-hr peaks of 0.3 and 0.2 μg/L, respectively. Similar data were also found in the San Joaquin River at Stockton during the same events. All of these concentrations exceeded the draft acute criterion for diazinon proposed by DF&G.

In contrast to the pulses observed on the San Joaquin River, diazinon concentrations at sites on the Old and Middle Rivers increased steadily from 0.04 to 0.15 μg/L during this same period (Kuivila 1993). These latter sites do not have as pronounced a downstream flow gradient and are heavily influenced by tidal movements. All of these measurements were ≥ the chronic criterion proposed by DF&G and some also exceeded the acute criterion.

Explain what this might mean to the food chain

In terms of toxicity, 100 percent mortality was observed with *C. dubia* exposed to samples collected daily from the San Joaquin River at Vernalis for 12 days following the first event (Kuivila 1993). Diazinon concentrations in these samples were ≥ 0.15 μg/L. Other pesticides, including chlorpyrifos, methidathion, and carbaryl may also have contributed to toxicity in these samples. No toxicity was observed in samples that contained ≤ 0.08 μg/L diazinon.

The USGS also monitored pesticides in the Sacramento River at Sacramento and in the San Joaquin River at Vernalis between 1 December 1993 and 28 February 1994 (MacCoy 1994). A total of 124 samples were collected, divided almost equally between the Sacramento River and San Joaquin Rivers. Diazinon was not detected in 26 percent of the samples collected from the Sacramento River. 34 percent of the samples exceeded the draft CDF&G 4-day average criterion (chronic) of 0.04 μg/L diazinon and 13 percent of the samples exceeded the 1-hr criterion (acute) of 0.08 μg/L. The results were very similar for the San Joaquin River; diazinon concentrations exceeded the draft chronic and acute water quality criteria in 44 and 16 percent of the samples, respectively, and was not detected in 33 percent of the samples. Chlorpyrifos was not detected (0.025 μg/L = D.L.) in any of the samples, but other pesticides were found, most notably simizine (to a maximum value of 1.7 μg/L) and methidathion (up to 1 μg/L). Generally, elevated concentrations of pesticides appeared in fairly distinct pulses that lasted between 3 and 10 days.

Interestingly, the amount of diazinon transported in the Sacramento River during these February events was much higher than in the San Joaquin River. Even though maximum concentrations were approximately 2.5 times higher at Vernalis than in the Sacramento River, flows in the Sacramento were 10 to 15 times greater than in the San Joaquin River (Kuivila 1994). Depending on the interactions between pesticide applications, rainfall events, and flow, much higher concentrations could be carried in the Sacramento River into the Delta. Since average flows in the Sacramento River in February between 1987 and 1991 were 12,800 cfs (CV=24.5%), compared with the 40,000-60,000 cfs that occurred during this study, it would appear that the potential exists for substantially higher concentrations to occur in the Sacramento River than measured in February of 1993.

This analysis is supported by data collected in February 1994 by DPR (V. Connor, RWQCB, personal communication). In this study, diazinon concentrations as high as 0.7 μg/L were measured in the Sacramento River following a rainfall event of 1.6 inches in four days. River flow rate was between 12,000 and 30,000 cfs during this period.

Menconi and Cox (1994) presented monitoring data for diazinon collected from 47 sites in the Sacramento-San Joaquin System between March 1991 and February 1993. A total of 340 samples were collected. Measured concentrations ranged between 0.01 and 36.8 μg/L diazinon. A total of 104 (30.6 %) samples exhibited diazinon concentrations that were less than the draft chronic water quality chronic crtierion. 170 of the samples (50 %) exceeded the acute criterion and the remainder exceeded the chronic criterion. All of the samples collected at Freeport/Rio Vista (n=4), Vernalis (n=6), Chipps Island/Martinez (n=3) exceeded the acute criterion of 0.08 μg/L.

In their water quality document for chlorpyrifos, Menconi and Paul (1994) presented monitoring data collected from sites in the San Joaquing system between March 1991 and February 1993. Of the 25 sites sampled, chlorpyrifos concentrations exceeded the criterion at 17 sites. Of the sites samples at least five times, only the Stanislaus River consistently exhibited chlorpyrifos concentrations less than the criterion. Six of the 45 samples collected from the San Joaquin River exceeded the LC50 for *C. dubia.* Concentrations as high as 0.35 μg/L were recorded from the San Joaquin River; this value exceeds the LC50s for *C. dubia* and *N. mercedis* by factors of 5 and 4, respectively.

Pesticides have also been associated with acute toxicity in municipal sewage treatment plants (Amato *et al.* 1992). Locally, metabolically activated organophosphorous pesticides were found to be responsible for acute toxicity to *C. dubia* in 10 of 14 toxic samples collected from a

150 mgd treatment plant that discharges into Suisun Bay (AQUA-Science 1992). Diazinon was identified as a primary toxic constituent and follow-up work with enhanced analytical detection limits showed that chlorpyrifos also contributed to toxicity.

Subsequent work on five POTWs that contribute a total daily flow of approximately 235 mgd to the Estuary suggests that the potential for toxicity due to pesticides may be widespread (Miller *et al.* 1994). Based on weekly samples collected for a 6-week period, all of the plants contained measurable levels of chlorpyrifos and diazinon in their influent and effluent streams. Four of the five plants contained at least one sample that had diazinon concentrations in excess of levels associated with acute *C. dubia* LC50s. Samples from three of the five plants contained chlorpyrifos at acutely toxic concentrations. The plants varied markedly in the removal efficiencies associated with the pesticides, particularly with respect to chlorpyrifos, which suggests that toxic concentrations may be treatable within the context of plant operation.

REFERENCES

1. AQUA-Science. 1992. Phase III toxicity identification evaluation studies with *Ceriodaphnia dubia.* Submitted to Central Contra Costa Sanitation Disctrict, Martinez, CA, 2 December 1992.

2. AQUA-Science. 1993. Sacramento Regional Regional Waste Water Treatment Plant Phase II Effluent Variability Study. Submitted to Sacramento Regional Wastewater Treatment Plant, Elk Grove, CA, 12 April 1993.

3. Bailey, H.C. 1993. Acute and chronic toxicity of the rice herbicides thiobencarb and molinate to opossum shrimp (Neomysis mercedis). Marine Environmental Research. 36:197-215.

4. Bailey, H.C., C. Alexander, C. DiGiorgio, M. Miller, S.I. Doroshov and D.E. Hinton. 1994. The effect of agricultural discharge on striped bass (Morone saxatilis) in California's Sacramento-San Joaquin drainage. Ecotoxicology, 3:123-142.

5. Bailey, H.C., C. DiGiorgio and D.E. Hinton. 1994. Trends in the toxicity of agricultural return waters to early life stages of striped bass (Morone saxatilis) and opossum shrimp (Neomysis mercedis). In: Western Wetlands, Selected Proceedings of the 1993 Conference of the Society of Wetland Scientists, D.M. Kent and J.J. Zentner, eds., Institute of Ecology, University of California, Davis, CA. pp. 83-89.

6. Department of Pesticide Regulation. 1994. Information on rice pesticides. Submitted to the Regional Water Quality Control Board. March 8, 1994. Department of Pesticide Regulation. Sacramento, CA.

7. Finlayson, B. J., J. M. Harrington, R. Fujimura, and G. Isaacs. 1991. Identification of methyl parathion toxicity in Colusa Basin Drain water. Environmental Toxicology and Chemistry. 12:291:303.

8. Foe, C. and V. Connor. 1989. 1989 rice season toxicity monitoring results (memorandum). Regional Water Quality Control Board, Sacramento, CA.

9. Foe, C. and V. Connor. 1991. 1989 rice season toxicity monitoring results. Regional Water Quality Control Board, Sacramento, CA.

10. Foe, C. and R. Sheipline. 1993. Pesticides in surface water from applicatins on orchards and alfalfa during the winter and spring of 1991-1992. Regional Water Quality Control Board, Central Valley Region, Sacramento, CA. 78 pp.

11. Hansen and Associates. 1994. Identification and control of toxicity in storm water discharges to urban creeks. Final Report submitted to Alameda County Urban Runoff Clean Water Program, 399 Elmhurst St., Hayward, CA.

12. Harrington, J.M. 1990. Hazard assessment of the rice herbicides molinate and thiobencarb to aquatic organisms in the Sacramento River system. Admin. Report 90-1. Environmental Services Division, California Department of Fish and Game, Sacramento, CA.

13. Kuivila, K., K.L. Crepeau, and J.L. Domagalski. 1992. Input and transport of selected alfalfa pesticides to the San Francisco Bay, CA (abstract). 13th Annual Meeting, Society of Environmental Toxicology and Chemistry. Cincinnati, Ohio. 9-13 November 1992.

14. Kuivila, K. 1993. Diazinon concentrations in the Sacramento and San Joaquin Rivers and San Francisco Bay. Open file report 93-440. U.S. Geological Survey, Sacramento, CA.

15. MacCoy, Dorene. 1994. Monitoring pesticide concentrations in the Sacramento and San Joaquin Rivers, California. Progress Report. U.S. Geological Survey, Sacramento, CA.

16. Menconi, M. and C. Cox. 1994. Hazard assessment of the insecticide chlorpyrifos to aquatic organisms in the Sacramento-San Joaquin River system (Draft). Admin. Report 94-2. Environmental Services Division, California Department of Fish and Game, Sacramento, CA.

17. Menconi, M. and S. Gray. 1992. Hazard assessment of the insecticide carbofuran to aquatic organisms in the Sacramento River system. Admin. Report 92-3. Environmental Services Division, California Department of Fish and Game, Sacramento, CA.

18. Menconi, M. and J.M. Harrington. 1992. Hazard assessment of the insecticide methyl parathion to aquatic organisms in the Sacramento River system. Admin. Report 92-1. Environmental Services Division, California Department of Fish and Game, Sacramento, CA.

19. Menconi, M. and A. Paul. 1994. Hazard assessment of the insecticide chlorpyrifos to aquatic organisms in the Sacramento-San Joaquin River system. Admin. Report 94-1. Environmental Services Division, California Department of Fish and Game, Sacramento, CA.

20. Miller, J.L., H.C. Bailey, and M.J. Miller. 1994. Fate and toxicity of diazinon and chlorpyrifos in municipal effluents (abstract). 15th Annual Meeting, Society of Environmental Toxicology and Chemistry. Denver, Colorado. 30 October-3 November 1994.

21. Norberg-King, T. J., E. J. Durhan, G. T. Ankley, and G. Robert. 1991. Application of toxicity identification evaluation procedures to the ambient waters of the Colusa Basin Drain, California. Environmental Toxicology and Chemistry. 10:891-900.

22. Segawa, R.T and N.J. Powell. 1989. Monitoring the pesticide treatments of the Japanese beetle project, Sacramento County, California, 1983-1986. Vol. III: Diazinon. Report No. EH 89-5. California Department of Food and Agriculture, Environmental Hazards Assessment Program, Sacramento, CA.

APPENDIX A

D-037167

Table 1. Application rates of molinate and thiobencarb and Sacramento River flows for the years 1970-1985.

	Application (lbs. X 1000)		
Year	Molinate	Thiobencarb	River Flow (cfs X 1000)
1970	490	na	7.0
1971	797	na	14.9
1972	656	na	8.2
1973	601	na	8.9
1974	457	na	12.7
1975	962	na	15.0
1976	760	na	8.4
1977	598	na	5.7
1978	1300	na	10.0
1979	1400	na	6.7
1980	1600	8	5.6
1981	1700	287	6.9
1982	1500	675	14.0
1983	930	351	23.1
1984	1500	353	6.7
1985	1100	475	5.4

na = not applied.

Table 2. Application rates of carbofuran and methyl parathion and Sacramento River flows for the years 1970-1988.

Year	Application (lbs. X 1000) Carbofuran	Methyl Parathion	River Flow (cfs X 1000)
1970	9	15	7.0
1971	9	30	14.9
1972	8	23	8.2
1973	11	32	8.9
1974	10	24	12.7
1975	5	23	15.0
1976	9	20	8.4
1977	21	17	5.7
1978	18	45	10.0
1979	29	67	6.7
1980	82	87	5.6
1981	108	100	6.9
1982	116	102	14.0
1983	73	54	23.1
1984	88	74	6.7
1985	58	48	5.4
1986	57	49	6.3
1987	57	57	6.9
1988	59	71	7.5

Ambient Toxicity

Comparatively few studies have investigated toxicity in ambient waters in the Bay/Delta system. In 1986, toxicity was noted in the Sacramento River at Sacramento using *Ceriodaphnia dubia* as the test organism (Foe and Connor 1991). In 1987, follow-up work suggested that much of the toxicity was related to seasonal discharges associated with rice culture and toxicity was found in the Sacramento River approximately 2 miles downstream of Colusa Basin Drain. Elevated mortality was also seen with fathead minnows exposed to water collected from this site. Similar results were obtained in 1988; however, toxicity was found both above and below Colusa Basin Drain which made it difficult to separate the sources of inputs. In 1989, monitoring with *C. dubia* at the end of May showed elevated mortalities at all sites on the river down to Rio Vista, 75 miles downstream of Colusa Basin Drain. One week later, elevated mortalities appeared to be limited to the stretch 30 miles downstream of the Drain (Foe and Connor 1991). Follow-up Toxicity Identification Evaluations (TIEs) conducted by EPA indicated that carbofuran and methyl parathion, two pesticides applied to rice, were responsible for toxicity to *C. dubia* in 1988 (Norberg-King *et al.* 1991). TIEs conducted on samples collected from CBD in 1989 suggested that carbofuran, methyl parathion, and malathion were responsible for toxicity to *C. dubia* (Norberg-King *et al.* 1989).

Bailey reported reduced survival of striped bass larvae exposed to one sample collected from the Sacramento River at Rio Vista on 15 May 1988 (Appendix B in Foe and Connor 1991). In 1989, two samples collected from the Sacramento River at Walnut Grove produced virtually complete mortality of larval striped bass within 96 hr. These samples were collected at the end of May and early June during the rice discharge season.

Finlayson *et al.* (1993) reported on the toxicity of samples collected from the Sacramento River at Rio Vista during rice season 1990. Three of the 30 samples tested significantly reduced the survival of *N. mercedis* within 96 hr. These samples were also tested with striped bass larvae but high and variable control mortalities made it problematic to assess the extent of toxicity to this species.

In late winter 1991-1992, eleven sites on waterways tributary to San Francisco Bay/Delta were monitored for toxicity associated with orchard run-off (Foe and Sheipline 1993). The sites were divided between the Sacramento and San Joaquin Basins. Six sites represented watersheds that ranged between 10,000 and 130,000 acres, with at least 10 percent of this total in orchards. The remaining five sites represented larger water bodies, including the Sacramento River, Feather River, Mokelumne River, Old River, and the San Joaquin River. Intermittent toxicity was observed in the smaller drainages during dry weather. However, all of these drainages exhibited toxicity during the period of precipitation that occurred between 4 and 20 February 1992. Of the larger water bodies, only the Mokelumne River exhibited toxicity during the dry period. However, once runoff occurred, samples from the Feather, Old and San Joaquin rivers also exhibited toxicity. Toxicity persisted in the San Joaquin River for some time following the storm. A total of 25 samples exhibited toxicity; in 22 cases, diazinon and/or methidathion were present at concentrations high enough to produce acute mortality. Concurrent monitoring data suggested that the San Joaquin river was acutely toxic for at least 8 days (12-19 February) and that this water reached as far north as Empire Tract and Venice Island before being diluted by flows from the Sacramento and Mokelumne rivers. These investigators concluded that the toxicity was largely due to the presence of pre-emergent pesticides, primarily diazinon, that had been applied to the orchards and were transported off-site in run-off from rain.

Toxicity associated with run-off from sites in the Delta that grew alfalfa was evaluated during March and April 1992 (Foe and Sheipline 1993). Intermittent toxicity was seen, particularly in Ulatis Creek, Bishop Tract Main Drain, and Paradise Cut. Analytical results indicated that both carbofuran and diazinon were present at potentially lethal concentrations in some of the samples. The authors felt that the data represented a "dry year" because no precipitation related run-off occurred during the study period.

Toxicity in samples collected primarily from Hog, Sycamore and Beaver Sloughs was evaluated with *C. dubia* in May and June 1994 (DiGiorgio *et al.* 1994). Samples were collected weekly from different sites, but only one of the 60 samples collected exhibited toxicity to *C. dubia.* This may have been a consequence of the time of sample collection; very little pesticide applications were occurring in these watersheds during the study period and no rainfall events occurred.

Delta sites were monitored twice monthly between May 1993 and May 1994, alternating between sites on the Sacramento and San Joaquin sides, using fathead minnows, *C. dubia,* and *Selenastrum capricornutum* (Deanovic *et al.* in prep.). Sampling sites included major river and through channels, back sloughs, island drains. The results, based on a preliminary analyses of the data, are summarized below:

Sacramento side	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY
No. tested	15	11	12	15	12	12	- -	12	- -	- -	13	12	12
No. toxic	7	5	6	7	8	4	- -	8	- -	- -	4	1	4
San Joaquin side													
No. tested	12	12	12	12	12	12	12	- -	12	- -	- -	12	13
No. toxic	5	9	5	3	1	5	2	- -	0	- -	- -	3	4

During most of the year, adverse effects were observed in approximately 33 to 75 percent of the samples with one, or more, of the test species. Months in which ≤ 10 percent of the samples toxic were April (Sacramento River side of the Delta) and September and January (San Joaquin side of the Delta). In most cases, toxicity was associated with the smaller creeks and sloughs and the Island drains. However, larger waterways were also frequently affected. In ten testing events conducted between May 1993 and May 1994, toxicity was found in samples collected in the Sacramento River (6 events), San Joaquin River (3 events at Vernalis and 5 events at Antioch), Old River (7 events), Middle River (1 event), and the Mokelumne River (5 events). The Port of Stockton site, which was considered to be dominated by urban inputs, exhibited toxicity in 4 events. Samples collected from the Delta-Mendota Canal also exhibited toxicity in 4 sampling events. These numbers would appear to be of concern; not only were the smaller creeks and sloughs affected, but also large masses of water moving through the Delta appeared to be contaminated as well.

Species sensitivity varied. In most cases, only one of the test species responded to a particular sample, implying that different toxicants were responsible. Based on a preliminary analysis, a total of 42 samples exhibited toxicity to *C. dubia,* 36 samples to fathead minnows, and 28 samples to *S. capricornutum.* Only 7 samples exhibited toxicity to both fathead minnows and

C. dubia and 6 samples exhibited toxicity to *C. dubia* and *S. capricornutum*. None of the samples exhibited toxicity to both the alga and fathead minnows.

Toxicity was also monitored during four rainfall periods (Bailey *et al.* in prep.). In the first period, 6-hr composite samples were collected over a two-day period at Green's Landing on the Sacramento River. One of the six samples collected exhibited toxicity to all three of the test species, including increased mortality in *C. dubia* and fathead minnows.

In the second period, samples were collected daily between 23 and 28 January 1994. 100 percent mortality was seen with *C. dubia* in samples collected from the San Joaquin River at Vernalis from 24 through 27 January. A follow-up TIE suggested that the mortalities were due to metabolically activated organophosphorous pesticides. The sample collected at Vernalis also reduced algal growth to approximately half of that seen on the four previous sampling days. No adverse effects were observed with *C. dubia* or the alga exposed to samples collected from the Sacramento River at Green's Landing during this same sampling event. However, growth was significantly reduced in fathead minnow larvae exposed to samples collected at Green's Landing 24 and 25 January.

A third series of tests evaluated toxicity at the same sites during another precipitation event (6-13 February 1994). Toxicity to *C. dubia* was apparent in samples collected 8-11 February at Vernalis. None of the samples collected at Vernalis exhibited toxicity to fathead minnows but the sample collected 9 February reduced algal cell numbers. One sample collected from the Sacramento River (11 February) exhibited toxicity to *C. dubia* and one sample also exhibited toxicity to fathead minnows (10 February). None of the samples collected from the Sacramento River exhibited toxicity to the alga.

Additional samples were collected from Vernalis between 17 and 23 February 1994. None of these exhibited toxicity to any of the three test species.

Samples were collected in the Sacramento river at Garcia Bend between December 1990 and November 1991 and tested for toxicity with *C. dubia* and fathead minnows (AQUA-Science

1993). Of the nine samples collected, 6 significantly increased mortality in the minnows tested. No adverse effects were noted with *C. dubia.* Between February 1992 and November 1992, the sampling site was switched to Freeport. Of 6 samples tested with fathead minnows, one produced elevated mortality and another reduced growth. Two of the samples also reduced the survival or reproduction of *C. dubia.* Three additional collections were made at Freeport between November 1993 and March 1994 and ambient toxicity evaluated with the 7-day fathead minnow test (AQUA-Science 1993 and 1994). No toxicity was observed in the sample collected in November, but survival and growth were adversely affected in the sample collected in February 1994. A follow-up sample collected in March also exhibited reduced survival.

EPA (1991) published a technical support document for water-quality based toxicity control. In this document, the Agency provides rationale for the development and application of water quality standards based on toxicity which are designed to protect aquatic communities. For acute toxicity, a maximum 1-hour exposure duration is permitted. For chronic or sublethal effects, the maximum allowable duration is 4 days. For both criteria, exceedences are permitted only once in 3 years, which gives the natural community a three year recovery period. The Agency also provides documentation that toxicity measured in samples with the standard EPA 3-species test[1], which was used to generate most of the data described above, should provide a level of detection within one order of magnitude of the most sensitive species found in the receiving water. Thus, while the absence of toxicity in the 3-species test does not necessarily mean that all organisms will be protected, the presence of toxicity strongly suggests that there will be effects on the receiving water biota.

How EPA's criteria relate to the Delta has not been established. However, the Agency's conclusions are based on a number of studies conducted by the EPA and independent investigators that relate toxicity to observed instream effects in both fresh and saltwater. These comparisons, which include data from over 200 sites, indicated that adverse effects could be predicted on the basis of toxicity in approximately 90 percent of the cases (EPA 1991). This high percentage of prediction, coupled with the diversity of sampling sites, suggests that this relationship is robust and should also apply in the Delta.

[1]Test species include *Ceriodaphnia dubia* (invertebrate), *Pimephales promelas* (fish), and *Selenastrum capricornutum* (alga). See EPA (1991b) for test procedures.

Clearly, toxicity occurs on a frequent basis in water samples collected from the Delta and its tributaries. In some cases, toxicity appears to be associated with rainfall events, while in other cases, toxicity can be related to local inputs. Toxicity may also be related to specific cropping practices, such as rice production, although recent data suggest that more restrictive pesticide use requirements have reduced toxicity associated with this particular crop (Bailey *et al.* 1994b). In any case, the frequency of toxicity suggests that EPA's guidance for maintaining water quality is being exceeded in the Delta much more frequently than the one event in 3 year interval estimated to be necessary to allow for recovery of an impacted system.

REFERENCES

1. AQUA-Science. 1993. Sacramento Regional Regional Waste Water Treatment Plant Phase II Effluent Variability Study. Submitted to Sacramento Regional Wastewater Treatment Plant, Elk Grove, CA, 12 April 1993.

2. Bailey, H.C. 1993. Acute and chronic toxicity of the rice herbicides thiobencarb and molinate to opossum shrimp (Neomysis mercedis). Marine Environmental Research. 36:197-215.

2. Bailey, H.C., C. Alexander, C. DiGiorgio, M. Miller, S.I. Doroshov and D.E. Hinton. 1994a. The effect of agricultural discharge on striped bass (Morone saxatilis) in California's Sacramento-San Joaquin drainage. Ecotoxicology, 3:123-142.

3. Bailey, H.C., C. DiGiorgio and D.E. Hinton. 1994b. Trends in the toxicity of agricultural return waters to early life stages of striped bass (Morone saxatilis) and opossum shrimp (Neomysis mercedis). In: Western Wetlands, Selected Proceedings of the 1993 Conference of the Society of Wetland Scientists, D.M. Kent and J.J. Zentner, eds., Institute of Ecology, University of California, Davis, CA. pp. 83-89.

4. DiGiorgio, C., H.C. Bailey, and D.E. Hinton. 1994. Delta water quality monitoring program: 2 May - 13 June 1994. submitted to U.S. Fish and Wildlife Service, Environmental Monitoring Branch, Sacramento, CA. Contract No. 10181-4-1823 (PM).

5. EPA. 1991. Technical support document for water quality based toxics control. EPA/505/2-90-001. Office of Water, U.S. Environmental Protection Agency, Washington, DC.

6. EPA. 1991b. Short-term methods for estimating the chronic toxicity of effluents and receiving waters to freshwater organisms. Third edition. EPA-600/4-91/002. Office of Research and Development, Cincinnati, OH.

7. Finlayson, B. J., J. M. Harrington, R. Fujimura, and G. Isaacs. 1991. Identification of methyl parathion toxicity in Colusa Basin Drain water. Environmental Toxicology and Chemistry. 12:291:303.

8. Foe, C. and V. Connor. 1989. 1989 rice season toxicity monitoring results (memorandum). Regional Water Quality Control Board, Sacramento, CA.

9. Foe, C. and V. Connor. 1991. 1989 rice season toxicity monitoring results. Regional Water Quality Control Board, Sacramento, CA.

10. Foe, C. and R. Sheipline. 1993. Pesticides in surface water from applications on orchards and alfalfa during the winter and spring of 1991-1992. Regional Water Quality Control Board, Central Valley Region, Sacramento, CA. 78 pp.

11. Norberg-King, T.J., E. Durhan and E. Makinen. 1989. 1989 Colusa Basin Drain Toxicity Identification Evaluation, Sacramento, California. National Effluent Toxicity Assessment Center Technical Report 09-89. U.S. Environmental Protection Agency, Environmental Research Laboratory, Duluth, MN.

12. Norberg-King, T. J., E. J. Durhan, G. T. Ankley, and G. Robert. 1991. Application of toxicity identification evaluation procedures to the ambient waters of the Colusa Basin Drain, California. Environmental Toxicology and Chemistry. 10:891-900.

Appendix 1. Delta Sampling Sites.

Major inputs to the Delta
- Sacramento river at Hood
- Mokelumne river at New Hope Rd.
- San Joaquin river at Vernalis

Smaller creeks and sloughs
- Ulatis creek
- French Camp slough
- Duck slough
- Lindsey slough
- Prospect slough
- Snodgrass slough
- Paradise Cut

Island Drains
- Ryer Island Main Drain
- Twitchell Island Main Drain
- Bouldin Island Main Drain
- Victoria Island Main Drain
- Pierson District Main Drain

Urban run-off dominated area
- Port of Stockton

Pathways of water through the Delta
- Sacramento river at Rio Vista
- Old river at Highway 4
- Old river at Tracy Blvd.
- Middle river at bullfrog
- Middle river at Tracy Blvd.
- Delta Mendota Canal